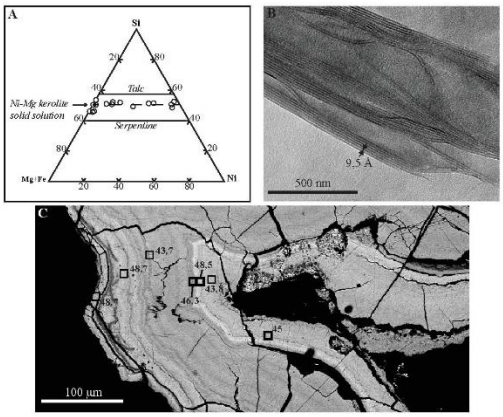
A raman spectroscopy study of the NI-MG kerolite solid solution: sensitivity of the O-H stretching vibrations to NI-MG substitution

Michel Cathelineau, Marie-Camille Caumon, Frédéric Massei, Matthieu Harlaux, David Brie

A RAMAN SPECTROSCOPY STUDY OF THE NI-MG KEROLITE SOLID SOLUTION: SENSITIVITY OF THE O-H STRETCHING VIBRATIONS TO NI-MG SUBSTITUTION. M. Cathelineau[1], M.-C. Caumon[1], F. Massei[1], M. Harlaux[1] and D. Brie[2], [1]Université de Lorraine, CNRS, CREGU, GeoRessources lab., BP 70239, F-54506 Vandoeuvre-lès-Nancy, France, [2]Université de Lorraine, CRAN, BP 70239, F-54506 Vandoeuvre-lès-Nancy, France

Introduction: The Ni-rich mineral phases forming the "garnierite" in the lateritic ore of the New Caledonian occurences are composed mainly in most cases by talc-like minerals, identified as kerolite. The Ni-Mg kerolite is a solid solution from Mg-kerolite to Ni-kerolite (pimelite) with a structure close to the one of talc. The interlayer distance is of ~9.5 Å but with an excess of Mg in octahedral site, a relative deficit of Si in tetrahedral site and a water content greater than the one in talc [1-4]. These minerals generally occur with a collomorph texture, marked by a chemical zoning with growing bands characterized by alternative Ni/Mg ratio. However, the structure of these minerals is still not elucidated. Indeed, they form generally poor crystallized mixtures, in particular with interstratified serpentines [2], which makes their study complex. Moreover, the Ni-Mg distribution in octahedral site may be heterogeneous or form clusters at a nanometric scale [5].

The preliminary studies of Villanova-de-Benavent et al. [6] and Cathelineau et al. [7] showed a high sensitivity of the OH stretching and the low wavenumber region to the different mineral phases (talc, serpentine, kerolite). Raman spectroscopy seems thus to be a performant tool to easily determine the mineral phases in a garnierite sample.

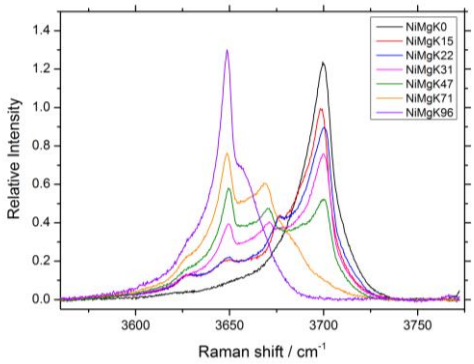


SEM, SEM-EDS and TEM analysis of Ni-Mg kerolite.

Objectives: In the present study we demonstrate the correlation between the chemical composition of the Ni-Mg kerolite and the vibrationnal spectra of the mineral, combining micro-analyses (TEM, SEM-EDS) and Raman microspectroscopy.

Materials & Methods: The kerolite samples from the Koniambo and Poro mines (New Caledonia) exhibit strong chemical zoning and cover the whole range of Ni-Mg substitution. Chemical composition is provided by SEM-EDS analyses, and confirmed by TEM. The absence of interstratification is checked by TEM. Raman spectra are acquired exactly at the point of the SEM-EDS chemical analysis. Data in the OH-stretchning region are treated both with classical decomposition using Gaussian-Lorentzian functions, but also by the BPSS algorithm [8,9], a chemometrics method aiming at solving the Multivariate Curve Resolution (MCR) also termed as Non-negative Matrix Factorization (NMF) in Signal Processing.

Results: A strong variation of the OH stretching band of kerolite is observed with Ni-Mg substitution with both conventional and chemometrics data treatment. With the increase of the Ni content, the band becomes more complex and shifted toward lower wavenumbers.

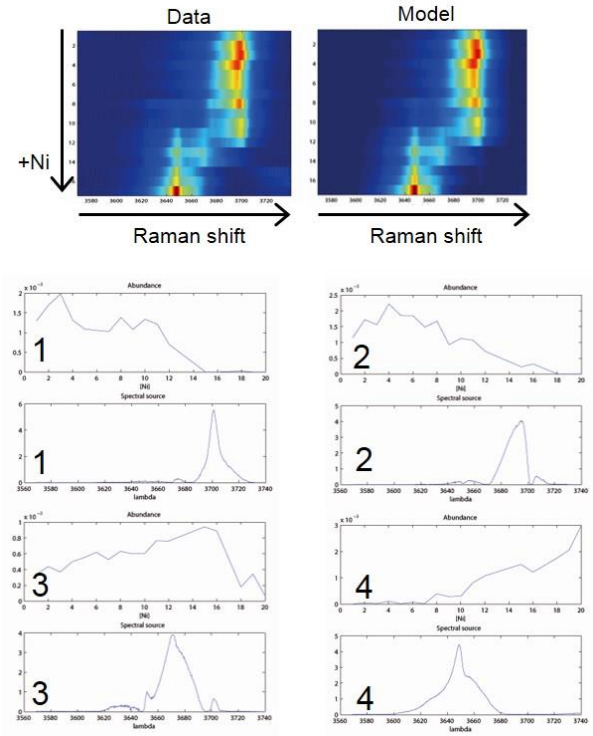


Raman spectra of kerolite as a function of Ni content. The number in sample name is the substitution rate of Mg by Ni.

Spectrum decomposition reveals at least two distinct spectra corresponding to the two end-members of the solid solution. Due to the complexity of the signal, intermediary compositions are not easily discriminated. Chemometrics treatment confirms the dependence of the Raman signal in the OH stretching region to the Ni-Mg substitution rate. It also reveals a mix of four distinct sources correlated to the Ni content.

The presence of four distinct species may be correlated to four different arrangements in octahedral sites: 3Mg, 2Mg-1Ni, 1Mg-2Ni, and 3Ni. The fact that the source corresponding to the highest Ni content appears at medium Ni content can be interpreted as an heterogeneous (cluster-like) distribution of Ni in the octahedral sheet. Finally, the strong difference between the simple

OH vibration spectrum of talc (one peak: one OH site) and the kerolite one lead to review the supposed OH arrangement in kerolite structure, with probably a higher number of OH sites.



BPSS data treatment of the Raman data in the OH stretching region. Each source is defined by a spectrum (bottom graph) and an intensity variation with Ni content (upper graph).

Conclusion: Raman microspectroscopy reveals to be a strong and usefull tool to identify kerolite in a garnierite sample at a micrometric scale, but also to determine the Ni-Mg substitution rate in the sample. The interpretation of the Raman spectrum in the OH stretching vibration range gives new inside the crystallographic structure of Ni-Mg kerolite.

[1] Wells MA, Ramanaidou ER, Verrall M, Tessarolo C. (2009). *Eur. J. Mineral.* 21, 467–83
[2] Villanova-de-Benavent C, Proenza JA, Galí S, Garcia-Casco A, Tauler E, et al. (2013). *Ore Geol. Rev.*
[3] Brindley GW, Bish DL, Wan H-M. (1979). *Am. Mineral.* 64, 615–25
[4] Manceau A, Calas G. (1985). *Am. Mineral.* 70, 549–58
[5] Manceau A, Calas G. (1986). *Clay Miner.* 21, 341–60
[6] Villanova-de-Benavent C, Aiglsperger T, Jawhari T, Proenza JA, Galí S. (2012) SEM-SEA, 180-181
[7] Cathelineau M, Harlaux M, Mosser-Ruck R, Caumon M-C, Boulvais P, et al. (2012) GeoRaman 10, 111-112
[8] Moussaoui S, Brie D, Mohammad-Djafari A, Carteret C. (2006) *Signal Process. IEEE Trans. On*. 54, 4133–45
[9] Moussaoui S, Carteret C, Brie D, Mohammad-Djafari A. 2006. *Chemom. Intell. Lab. Syst.* 81, 137–48